

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

NO DRAWINGS

Dental Prostheses

We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of Leverkusen-Bayerwerk, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to dental prostheses and to an improved process for producing the same. More particularly, the invention relates to the provision of trans-
parent dental prostheses which possess good
15 strength characteristics and very extensive processability, via the so-called "powder-liquid process".

It is known in dental technology, that dental prosthese may be produced by a
20 method known as the powder-liquid process (see German Patent Specification No. 737,058 and United States Patent Specification No. 2,122,306) by curing a mixture of about three parts of a finely-divided bead
25 polymer, consisting largely of combined methyl methacrylate, and one part of monomeric methyl methacrylate at an elevated temperature and in the presence of a catalyst such as benzoyl peroxide,
30 within a two-part denture flask of gypsum which serves as the mold.

Modifications of this basic process have also been described heretofore in which resins, plasticizers or dyestuffs are added to the polymer employed, and copolymers,
35 for example, are used in place of the homopolymer of methyl methacrylate, the copolymers consisting of a major portion of combined methyl methacrylate and also
40 containing other combined vinyl compounds, vinylidene compounds or divinyl compounds as the second component.

It is further well established as of this

date that the processing properties of the prostheses may be improved by employing, 45 in lieu of the single species powder with the above-mentioned additives in the powder-liquid process, mixtures of at least two polymers as the powder, wherein these differ in respect of their mean particle size. 50 For example, one of the powder components might consist of a homopolymer of methyl methacrylate and the other powder component of a copolymer of methyl methacrylate, the mean particle size of the 55 homopolymer component being adjusted to insure that it is greater than the mean particle size of the copolymer component. Suitable copolymers thus employed consist of methyl methacrylate polymers containing 60 acrylic acid esters of lower alcohols, butadiene, and esters of methacrylic acid as the comonomers, and for this purpose the esters of methacrylic acid should be esters of alcohols containing more than 4 carbon 65 atoms (see German Patent Specification No. 940,493).

If, in the liquid, monomers are employed which differ substantially from the methacrylic acid methyl ester, difficulties may be encountered, for example, with respect to the remaining monomer not consumed in the polymerisation process, by reason of its physiological properties. In addition, if, for example, repair of a prosthesis becomes 75 necessary or desirable, monomeric methacrylic acid methyl ester-containing materials are usually utilized. Prostheses made of styrene-containing polymers are, as is now well established, quite apt to form 80 capillary cracks.

It is significant to note that, despite the aforementioned modifications of the powder component, no dental prostheses have yet been obtained which are fully 85 satisfactory from the points of view of

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cosmetic criteria, and processing requirements.

Still other processes have been described, the intent of which is to satisfy the high requirements made in respect of dental prostheses, in which other monomers are added to the methyl methacrylate employed as the liquid in the powder-liquid process. Thus, for instance, it is known that the strength properties, cosmetic properties, and general processing characteristics may be improved by the addition of monomers such as the esters formed from acrylic and methacrylic acids with alcohols containing from 8 to 10 carbon atoms, or by the addition of cyclohexyl methacrylate, methoxyethyl methacrylate, butoxyethyl methacrylate, tetrahydrofurfuryl methacrylate or dichlorostyrene. However, even the addition of all of these additives have proved insufficient for the production of dental prostheses by the powder-liquid process which satisfy the above requirements, in every respect. For example, a particular disadvantage stems from the fact that the above additives cannot prevent the prostheses from becoming opaque or non-transparent at locations where their wall thickness is necessarily low. As a result, failure to detect faults which might have developed during manufacture of the prostheses is possible.

It is the object of the present invention to provide a process for the production of transparent dental prostheses possessing very good consumer properties, good strength characteristics and very extensive processability.

According to the present invention in a process for the production of dental prostheses by the powder-liquid process the liquid comprises a mixture of methyl methacrylate and a methacrylic acid amide and/or acrylic acid amide containing in its molecule at least one free hydroxyl group and/or an ether group.

By methacrylic and acrylic acid amides containing in the molecule at least one free hydroxyl group is meant methacrylic and acrylic acid amides in which one or both hydrogen atoms of the amide group is or are substituted by lower alkyl radicals, having usually not more than four carbon atoms, which carry one or more OH groups. Examples of these are N-hydroxymethyl acrylamide and methacrylamide, N-(2-hydroxyethyl)-acrylamide and methacrylamide, N-(2-hydroxypropyl)-methacrylamide, N-(3-hydroxypropyl)-methacrylamide, N-(2, 3-dihydroxypropyl)-methacrylamide, and N,N-bis-(2-hydroxyethyl)-methacrylamide. The carbon chain may also contain ether bridges, such as for example in N-(hydroxyethyl-oxyethyl)-methacrylamide.

The OH groups may also be etherified, for example with methyl or ethyl groups. N-methylolmethacrylamide methyl ether and N-2-hydroxyethyl-methacrylamide ethyl ether may be mentioned as examples.

Preferably at least 40% by weight of methyl methacrylate is employed in the prosthesis mixture. Unsaturated polymerisable acids or anhydrides thereof can also be added to the liquid monomer or to the polymer.

The foregoing liquid is optionally used with a suitable cross-linking agent, being a compound containing at least two olefinic polymerisable double bonds in its molecular configuration.

The quantity of the hydroxy- or ether-component employed varies in relationship to the particular compound employed, but it is preferably within the range of from 5 to 50 percent by weight of the total weight of liquid.

The optional third component of the liquid, namely the cross-linking agent, is added to the mixture in a proportion of from 0.5 to 20 percent by weight, and preferably within the range of from 2 to 10 percent by weight. Suitable cross-linking agents include, for example, glycol diacrylate, divinylbenzene, triacryl-formal, glycerine triacrylate and glycerine trimethacrylate.

Curing of the shaped product in the gypsum mold is generally effected in accordance with conventional practice, with the addition of a polymerisation catalyst capable of forming free radicals, for example, benzoyl peroxide, in a water bath maintained at approximately 100°C.

Particularly good results are achieved in accordance with the process of the invention when a mixture of two polymers is employed as the powder. For this purpose, the mixture should preferably consist of a homopolymer of methyl methacrylate and a copolymer of methyl methacrylate, and the mean particle size of the homopolymer should be larger than the mean particle size of the copolymer.

Pursuant to the process of the invention, it is often not necessary to cure the molded product in the gypsum denture flask within a water bath maintained at 100°C., since transparent prostheses may be obtained when the curing or polymerisation of the gypsum denture flask is effected in a drying cabinet. Such a procedure with the conventional mixtures has the tendency of forming much more intense opacities.

The following Examples are given to illustrate the invention. The ratio of parts by weight to parts by volume has the same relationship as have grams to millilitres.

EXAMPLE I

3 parts by weight of a mixture containing 80 weight percent of a bead homopolymer

- of methyl methacrylate having a mean bead diameter of 0.09 mm and a (η) value of 1.0 and 20 weight percent of a bead copolymer containing 80 weight percent of combined methyl methacrylate and 20 weight percent of combined ethyl acrylate, having a mean bead diameter of 0.05 mm and a (η) value of 1.0, are mixed with 0.01 parts by weight of benzoyl peroxide and 1 part by volume of monomeric methyl methacrylate. After swelling, the mixture is thoroughly kneaded and a prosthesis mould is a two-part plaster flask is lined with the resulting paste. The plaster mould had previously been lined with a 2% aqueous solution of sodium alginate. The closed flask is then inserted in a water bath at 20°C, the temperature of the bath then being raised to 100°C over a half hour period and maintained for half an hour at this temperature. The plastic moulding removed from the mould after cooling has a milky turbidity which is increased still further after exposure to the air for a few days.
- If, however, the above procedure is repeated, using, instead of the monomeric methyl methacrylate, 1 part by volume of a mixture of 50-80 parts of methyl methacrylate and 50 to 20 parts of N-(2-hydroxyethyl)-methacrylamide, the milky turbidity increasingly disappears with increasing addition of the new liquid component.

EXAMPLE II

- If the polymer mixture described in Example 1, is used in accordance with that Example with 1 part by volume of a mixture of 50-90 parts of methyl methacrylate and 50- to 10 parts of N-methylolmethacrylamide monomethyl ether, prostheses are obtained which are largely free from the above described milky turbidity.

WHAT WE CLAIM IS:—

1. A process for the production of dental prostheses by the powder-liquid process in which the liquid comprises a mixture of methyl methacrylate and a methacrylic acid amide and/or acrylic acid amide containing in its molecule at least one free hydroxyl group and/or an ether group.
2. A process as claimed in claim 1 wherein the methyl methacrylate comprises at least 40 per cent by weight of the prosthesis mixture.
3. A process as claimed in claim 1 or 2 wherein the liquid also comprises a small

amount of a cross-linking agent containing in its molecule two unsaturated double bonds capable of being polymerized.

4. A process as claimed in any of claims 1 to 3, wherein the methacrylic acid amide and/or acrylic acid amide comprises from 5 to 50 percent by weight of the total weight of liquid.

5. A process as claimed in any of claims 1 to 4 wherein the cross-linking agent comprises from 0.5 to 20 percent by weight of the total weight of liquid.

6. A process as claimed in any of claims 1 to 5 wherein the free hydroxyl group-containing compound is N-hydroxymethyl acrylamide, N-hydroxymethyl methacrylamide, N-(2-hydroxyethyl)-acrylamide, N-(2-hydroxyethyl)-methacrylamide, N-(2-hydroxypropyl)-methacrylamide, N-(3-hydroxypropyl) methacrylamide, N-(2,3-dihydroxypropyl) methacrylamide, or N,N-bis-(2-hydroxyethyl) methacrylamide.

7. A process as claimed in any of claims 1 to 5 wherein the free hydroxyl group-containing compound is N-(hydroxyethyl)-oxyethyl)-methacrylamide.

8. A process as claimed in any of claims 1 to 5 wherein the ether group-containing compound is N-methylolmethacrylamide methyl ether or N-2-hydroxyethyl-methacrylamide ethyl ether.

9. A process as claimed in any of claims 1 to 8 wherein a mixture of two polymers consisting of a major proportion of methyl methacrylate having different mean particle sizes is employed as the powder.

10. A process as claimed in claim 9, wherein the powder consists of a mixture of a homopolymer of methyl methacrylate and a copolymer of methyl methacrylate the mean particle size of the homopolymer being relatively large and the mean particle size of the copolymer being relatively small.

11. A process for the production of dental prostheses substantially as hereinbefore described in Example 2.

12. Dental prostheses whenever prepared by a process according to any one of claims 1 to 11.

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